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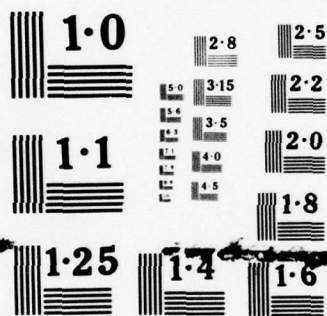
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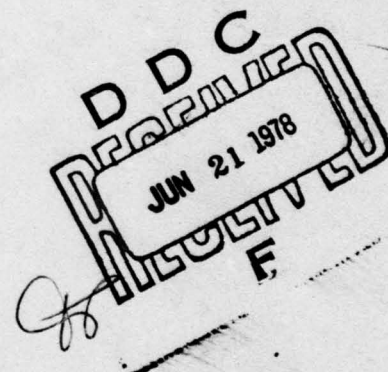
PIEZO-OPTIC PROPERTIES OF LIQUIDS UNDER HIGH PRESSURE

Final Report

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Physics Program, Code 421
Office of Naval Research
Arlington, Virginia 22217

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1. INTRODUCTION

On May 1, 1975 a new program was initiated under the sponsorship of the Office of Naval Research (Physics Program) to carry out a systematic study on piezo-optic properties of liquids under high pressure. Significant progress has been made in this program and in what follows, a brief summary of the work accomplished to date is presented.

2. WORK ACCOMPLISHED

The technique of high pressure-optical interferometry which has been developed and successfully employed by the author and his students for studies on the piezo-optic properties of solids, has now been adapted for similar studies on liquids. Measurements on the variation of the refractive indices of a number of liquids at room temperature have been completed. The results obtained have already been published in the form of two short articles in Physical Review Letters and another in Review of Scientific Instruments. Three articles have already been submitted for publication in Journal of Chemical Physics and in the Proceedings of the sixth AIRAPT International Conference on High Pressure. Copies of these three articles are attached as appendices to this report. Hence, in what follows only some of their highlights are mentioned.

A high-pressure liquid cell interferometer has been designed and constructed for precision interferometric measurement of the variation of refractive index, Δn , of liquids with pressure, P . The amount of liquid needed is only 3 ml. Such precision interferometric measurements at high pressures have been carried out on CCl_4 , n-pentane, n-hexane, n-heptane, n-octane, n-nonane, n-decane, benzene, chloro-benzene, methyl alcohol, and water at room temperature. Since most of these liquids freeze at room temperature even before 14 kbars is reached, the measurements were carried out up to the freezing point or 14 kbars, whichever pressure is lower.

In every case the refractive index was found to increase with pressure with pronounced nonlinearity. In the case of solids like alkali halides, Vedam and his coworkers (1969) have reported that though Δn vs. P is nonlinear, the same data show perfect linear relationship between Δn vs. P is nonlinear, the same data show perfect linear relationship between Δn and the volume strain $\Delta V/V_0$. Correspondingly, in the case of liquids, the observed pronounced nonlinearity between Δn and P could be reduced significantly when Δn is plotted as a function of the volume strain, which was computed with the help of the various equations of state reported in the literature. It was found that the nonlinearity observed for Δn is considered as a function of Lagrangian strain, η ; and in the case of the Eulerian strain ϵ , the nonlinearity practically disappeared. This was found to be true in all liquids irrespective of the size, shape, polar, or nonpolar nature of the molecules as well as the equation of state used to compute the volume strain.

Since a linear relation between Δn and ϵ has been found, this linearity criterion was used to discriminate between the various equations of state prevalent in the literature using a least-squares analysis. It was found that 2nd-order Birch, 2nd-order Murnaghan, and Keane's equations of state give the best fit for every liquid considered. It should be mentioned that this is the first time these equations of state were subjected to such rigorous curve-fittings tests involving literally hundreds of data points spread out through the entire range of pressure or strain. Anderson (1968) and Chhabildas and Ruoff (1969) have shown that the Birch and Murnaghan equations yield physically unrealistic results at very high pressures and hence are not recommended for extrapolation for high pressures. The Keane equation, which does not suffer from such a drawback, was used for further studies. It may also be mentioned that since the same equations of state are employed both for solids and liquids, it is believed that the present conclusion on the usefulness of Keane's equation of state will be of value for solid-state and geophysicists as well.

Next, the various expressions prevalent in the literature for the relationship between refractive index and density were analyzed. It was found that in general all the equations give fairly good fits at very low pressures but as the pressure is increased the disagreement between theory and experiment becomes more and more prominent in almost all cases except for the Kirkwood-Brown and Omini equations. Furthermore, it is shown that the Kirkwood-Brown equation yields values of Δn slightly smaller than the observed values implying a small increase in polarizability with increasing density, which is not quite consistent with the variation of polarizability in gases and solids. On the other hand, the Omini equation yields values of Δn which are slightly larger than the experimentally observed values implying a small decrease in polarizability with increasing density. Further work on the theoretical and experimental aspects of the subject will be necessary before a definite statement in the variation of polarizability with density of liquids can be made.

2.1 Publications

1. Piezo-optic Behavior of Water and Carbon Tetrachloride Under High Pressure: By K. Vedam and P. Limsuwan, Phys. Rev. Letts. 35, 1014 (1975).
2. Optical Interferometry in Liquids at High Pressures to 14 kbars: By K. Vedam and P. Limsuwan, Rev. Sci. Instruments, 48, 245, 1977.
3. Piezo- and Elasto-Optic properties of Liquids under High Pressure. I. Refractive Index vs Pressure. Pichet Limsuwan and K. Vedam. (Submitted to Journal Chem. Phys.)
4. Piezo- and Elasto-Optic properties of Liquids under High Pressure. II. Refractive Index vs Strain (Submitted to Journal Chem. Phys.)
5. Piezo-optic Behavior and the Equation of State of Liquids. K. Vedam and Pichet Limsuwan, Proc. Sixth AIRAPT Int. Conf. on High Pressure, Boulder, Colo. (1977).

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2.2 Oral Presentation at Scientific Meetings

1. Piezo-optic Behavior of the Equation of State of Liquids: By. P. Limsuwan and K. Vedam, presented at the "Washington Area High Pressure Colloquium" at the U.S. Naval Academy, Annapolis, Maryland, October 13, 1976.

2. Piezo-optic behavior and the Equation of State of Liquids by K. Vedam and Pichet Limsuwan, at the Sixth AIRAPT International Conference on High Pressure, Boulder, Colo., July 25-29, 1977.

2.3 Reports Submitted

1. Piezo-optic Properties of Liquids Under High Pressure. Report No. MRL-KV-75-1 dated December 22, 1975.

2. Piezo-optic Properties of Liquids Under High Pressure. Report No. MRL-KV-76-1 dated December 15, 1976.

2.4 Theses, Degrees Granted

Pichet Limsuwan, Ph.D. in Physics, Pennsylvania State University, March 1978, Thesis on "Piezo-optic Properties of Liquids Under High Pressure"

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Piezo-and Elasto-Optic Properties of Liquids under High Pressure

I. Refractive Index vs. Pressure *

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ABSTRACT

The variation of the refractive index of liquid with pressure to 14 kbars has been determined by an optical interferometric method. The liquids studied are carbon tetrachloride, n-pentane, n-hexane, n-heptane, n-octane, n-nonane, n-decane, benzene, chlorobenzene, methyl alcohol, and water at room temperature. Since most of these liquids freeze at room temperature even before 14 kbars is reached, the measurements were carried out up to the freezing point or 14 kbars whichever pressure is lower. In every case the refractive index increases with pressure with pronounced nonlinearity, particularly at high pressure.

* Research work supported by Office of Naval Research (Physics Program).

Introduction

A glance at the literature⁽¹⁻²⁴⁾ reveals that the number of liquids on which piezo-optic measurements have been reported is indeed very few, and amongst them the number of liquids on which such measurements have been carried out by two or more investigators (so that an intercomparison can be made) is even fewer--in fact, the number is not even ten! Furthermore, when the actual comparison is made, one finds that the values of the elasto-optic coefficient $\rho(dn/dp)$ differ by at least 2% in almost every case, and in some cases the difference is as high as 5% (here ρ is the density). This will become evident by a glance at the two recent compilations by Riley and Klein⁽²⁰⁾ and Uchida.⁽²¹⁾ It should be mentioned, however, that the former table contains a few typographical errors--still it does not alter the above conclusions. The reasons for this great disparity amongst results obtained are not far to seek. These elasto-optic coefficients have been obtained experimentally by two methods: (i) one is the measurement of the change in the refractive index, Δn , by pressure either directly by interferometry or by the measurement of the refractive index itself at various pressures and then evaluating the Δn . The latter approach obviously is susceptible to large errors since Δn is obtained as a small difference between two large quantities; (ii) the second method is based on the diffraction of light by ultrasonics. This, in most cases, is an indirect method because of the difficulty in measuring and calculating the acoustic power or pressure at the acousto-optic interaction region. Nevertheless, if an appropriate standard material is available one can evaluate the

elasto-optic coefficient by comparison of the intensities of the diffracted light from the material and the standard medium. But during this process numerous assumptions are tacitly made, such as the constancy of temperature as well as the acoustic power at the interaction region, negligible acoustic absorption in both the materials, etc.-- and these assumptions are certainly not valid in every case. Furthermore, since the compressibility of a liquid is quite different under adiabatic and isothermal conditions, the piezo- and elasto-optic coefficients also will be different in the two cases. This fact has really not been appreciated by all the workers in this field. The interferometric method, besides yielding the results directly, is naturally the most accurate method and this technique has indeed been employed by the very early workers as well as by Waxler and Weir⁽¹⁵⁾ recently, the latter up to a maximum pressure of only 1.1 kbars.

Recently the authors^(25, 26) have designed and constructed a suitable high pressure optical liquid cell interferometer and with that it has been possible to carry out precision optical interferometric measurements with a number of liquids such as water, carbon tetrachloride, n-pentane, n-hexane, n-heptane, n-octane, n-nonane, n-decane and chlorobenzene, right up to their high pressure-freezing points 14 kbars or whichever is lower. The results obtained exhibit many interesting nonlinear piezo-optical effects and these are presented and discussed in this and the following articles.

Experimental

Since the experimental details have been discussed in detail in an earlier article⁽²⁶⁾, it will not be described here. Suffice to say that the liquid cell interferometer based on the principles of Newton's rings, is of such design that it could be inserted in a 14 kbar high pressure optical vessel⁽²⁷⁾. The maximum amount of experimental liquid necessary for these measurements is only 3 cc. The temperature of the liquid inside the pressure vessel was maintained to within 0.1°C and thus corrections for thermal fluctuations are not needed.

The change in the refractive index Δn of the liquid was evaluated from the well known interference formula

$$\Delta n = (\Delta f \lambda - 2n\Delta t) / 2t_0 \quad (1)$$

where Δf is the number of fringes shifted, t_0 the initial thickness of a vitreous silica spacer between the planoconvex lens and the optical flat of the interferometer, Δt the change in thickness of the spacer due to hydrostatic pressure, and λ the wavelength of light employed. In actual practice, the values of Δn and Δt at each pressure, corresponding to some known fringe shift, were evaluated by a programmed calculation on the IBM 370/68 computer. The value of n was corrected by this Δn before it was used for the computation of $\Delta n'$ for the next fringe shift.

The change in thickness of the vitreous silica spacer Δt was evaluated with the help of the nonlinear theory of elasticity developed by Murnaghan⁽²⁸⁾, Birch⁽²⁹⁾, and Barsch⁽³⁰⁾. According to this theory,

for an isotropic solid such as vitreous silica, the pressure P is related to the strain by

$$P = -(C_{11} + 2C_{12})\eta + (C_{11} + 2C_{12} - \frac{1}{2}C_{111} - C_{123})\eta^2 \quad (2)$$

where η , the Langrangian strain is given by

$$\eta = \frac{(t_0 + \Delta t)^2 - t_0^2}{2 t_0^2}, \quad (3)$$

C_{ij} and C_{ijk} are the second- and third-order elastic constants and t_0 is the initial thickness. Thus, since data on second- and third-order elastic constants for vitreous silica are available, Eqns. (2) and (3) can be used to evaluate Δt the change in the thickness of the spacer and hence Δn the change in refractive index of the liquid.

The volume strain of an isotropic material is related to the Langrangian strain by the relation

$$\eta = \frac{1}{2} \left[\left(\frac{V}{V_0} \right)^{2/3} - 1 \right] \quad (4)$$

By rearrangement of Eqn. (4) we have

$$\frac{\Delta V}{V_0} = \frac{V - V_0}{V_0} = (1 + 2\eta)^{3/2} - 1 \quad (5)$$

where $\frac{\Delta V}{V_0}$ is the volume strain.

The volume strain of a material can also be expressed as a function of applied hydrostatic pressure as

$$\frac{\Delta V}{V_0} = -aP + bP^2 \quad (6)$$

where a and b are temperature sensitive constants. These coefficients are related to the bulk modulus B and its pressure coefficient according to

$$a = \frac{1}{B}, \quad (7)$$

$$b = \frac{1}{2B^2} \left[\left(\frac{\partial B}{\partial P} \right) + 1 \right] \quad (8)$$

Hence from the values of a and b given in the literature for vitreous silica, the values of Δt of the vitreous silica can also be evaluated at each pressure with the help of Eqns. (6), (5), and (3) and thence Δn from Eqn. (1).

It is evident that since large pressures and hence large strains are involved in these measurements, Δf the number fringes shifted, Δt the change in the thickness of the spacer and Δn the change in refractive index of the liquid are all nonlinearly related to the pressure. It can be shown by slight manipulation of Eqn. (1) with the help of nonlinear theory of elasticity, that, Δn the change in refractive index involved during one additional fringe shift after m fringes have shifted, is given by

$$\Delta n = n_{m+1} - n_m = \frac{[f_{m+1} - f_m] \lambda}{2t_0 (1 + \eta_{m+1})} - \frac{n_m [\eta_{m+1} - \eta_m]}{(1 + \eta_{m+1})} \quad (9)$$

The advantage of this form over Eqn. (1) is that t_0 appears only in the first term on the right-hand side, thus if several different spacers are used in the measurements for a particular liquid, one could use all the data by normalizing the thickness of the spacers, i.e., by determining f/t_0 as a function of pressure. In other words, all the experimental data

can be made by least-squares technique, to fit an equation of the form

$$f/t_0 = AP + BP^{1/2} + CP^{1/3} + \dots \quad (10)$$

where A, B, C,... are constants and P is the pressure. The value of Δn can be evaluated from Eqn. (10) at any pressure from the value of f/t_0 . It should be noted, however, that this curve fitting technique is not valid if the liquid under study goes through a phase transition in the pressure range employed.

Liquids Studied

The pressure dependence of the refractive index of twelve liquids has been studied in the pressure range 20-30°C. The liquids chosen for this investigation are composed of molecules of widely varying size, symmetry and shape; namely, CCl_4 , n-decane, n-nonane, n-octane, n-heptane, n-hexane, n-pentane, benzene, chlorobenzene, toluene, methyl alcohol, and water. All these liquids except water were analytical reagent grade of highest purity commercially available materials and did not require any further purification. The water employed was freshly distilled and deionized water.

In order to ascertain the purity of the materials, as well as the reliability of the published data on the refractive index of liquids, the refractive indices were first measured to the fifth decimal place with a Bausch & Lomb, Abbe-type precision refractometer and the results were compared with those given in the literature. Table I gives the measured values of the initial refractive indices for all the liquids

tested and the published data for the corresponding liquids. It is seen that the agreement between these values is quite satisfactory in all cases except where the values reported in the literature had to be interpolated. Even though such interpolation was carried out with the help of a computer by least-squares analysis using polynomial fit, the agreement is far from satisfactory. Hence in the analysis and interpretation of our experimental results on piezo-optic measurements, the values of n_o measured by us were employed.

Results and Discussion

The various relevant parameters of the experimental results are given in Tables II and III. Table II lists the coefficients A, B, C,... of Eqn. (10) for the various liquids studied at the listed temperatures. These temperatures correspond to those at which P-V data on the liquid under study are available in the literature. From the values of the coefficients A, B, C,... given in Table II, one can easily compute the normalized total number of fringe shifts at any pressure. In other words, this table provides a summary of the raw experimental data and hence can be utilized for detailed analysis and interpretation when better experimental P-V data become available.

Table III lists the initial value of the refractive index n_o , the total number of fringes observed to shift with increasing pressure from one atmospheric pressure to the maximum pressure, and also Δn the total measured change in the refractive index of the liquid. For all liquids measured except n-pentane and methyl alcohol, the

maximum pressures listed were determined by the freezing of the liquid at the stated temperature.

The second- and third-order elastic constants of vitreous silica as determined by Bogardus⁽³⁸⁾ were used to evaluate the change in thickness, Δt , of the spacer. Thus the corresponding changes in refractive index, Δn , of the liquid were evaluated with the help of Eqns. (1) and (10) and are given in Table III. According to Bogardus, $C_{11} = 7.839$, $C_{12} = 1.587$, $C_{111} = 52.5$, $C_{112} = 23.9$ and $C_{123} = 5.4$, where all constants are given in units of 10^{11} dyne/cm². As mentioned earlier, Δt can also be evaluated from compressibility data on vitreous silica. According to Adams and Gibson⁽³⁹⁾, the coefficients a and b of Eqn. (6) are 2.689×10^{-6} (bar)⁻¹ and -2.08×10^{-11} (bar)⁻², respectively, for vitreous silica at 25°C. The corresponding changes in refractive index evaluated from these values are also given in Table III. The difference of Δn evaluated from the elastic constant data of Bogardus and that evaluated from the compressibility data of Adams and Gibson becomes maximum at the maximum pressure. For example, for n-pentane, the values of Δn so evaluated are 0.1825_0 and 0.1817_8 , respectively, at 14 kbar, i.e., 0.4% difference in the values of Δn is noticed. However, in view of the greater accuracy claimed in the more recently determined elastic constants data of Bogardus, they will be used in the discussion in this and the following papers.

The variation of the refractive index of CCl_4 , n-decane, n-nonane, n-octane, n-heptane, n-pentane, benzene, chlorobenzene, toluene, methyl alcohol and water with pressure are shown in Figures 1 to 4. It is seen that in every case the refractive index increases with pressure

with pronounced nonlinearity, particularly at high pressures. Since all the earlier reported measurements on liquid were limited to pressure less than 1.5 kbars, the nonlinear behavior was not noticed.

Table IV lists the values of Δn the variation in the refractive indices of a few liquids at high pressures reported in the literature along with our results at the corresponding pressures. It is seen that excellent agreement to within 1×10^{-4} is obtained in every case except with the results of Rosen on water. Rosen measured the refractive index of water at various pressures by the minimum deviation method with the help of a pressure vessel in the shape of a prism. Since the change in refractive index is obtained as a small difference between two large quantities in this technique, the accuracy attained is not as high as in the interferometric method employed by Waxler and Wier as well as in the present work.

Amongst the liquids studied here, only the normal alkanes form a homologous series and hence form a group of liquids whose properties can be compared meaningfully. It is well known that in the n-alkanes which are in the liquid phase at room temperature n-pentane has the lowest melting point, the lowest boiling point and the lowest density. Further as the number of carbon in the alkanes increases the molecular weight, the density, the melting point and the boiling point increase progressively. From Table III it is seen that n-pentane has the lowest initial refractive index n_0 , has the largest range of pressure in which it is stable as liquid (freezing pressure greater than 14 kbars at 25°C), correspondingly largest number of fringes observed to shift and the largest observed change in refractive index Δn_{\max} . Again, as

we move up the homologous series a systematic and progressive variation is noticed in n_0 , the freezing pressure, the maximum number of fringes observed to shift and in Δn_{\max} .

The results of the present measurements can be utilized to study the extremely interesting relationship between refractive index and density of the liquids and thus to answer the fascinating question whether the electronic polarizability of the molecule is constant or not. But before such an analysis can be made one should know the P-V relationship of the liquids under study. An examination of the literature reveals that reliable experimental P-V data on liquids over a wide pressure range are indeed sparse and further numerous empirical and semi-empirical equations of state have been proposed to describe the data. Our own studies on the piezo-optic properties of liquids indicate that these piezo-optic data themselves can be used to discriminate between the various equations of state and possibly arrive at one generalized equation with minimum number of adjustable parameters applicable for all liquids. This is discussed in the following articles⁽⁴⁰⁾.

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Table I. Index of refraction of twelve liquids relative to air at λ 546.1 nm.

Liquid	Temp. (°C)	n_0		
		Present Work	Literature	Reference
CCl_4	25	1.45951	1.46085*	(31)
n-Decane	25	1.41138	1.41216*	(32)
n-Nonane	25	1.40499	1.40482	(33)
n-Octane	25	1.39682	1.39786*	(34)
n-Heptane	25	1.38682	1.38675	(33)
n-Hexane	25	1.37508	1.37468*	(34)
n-Pentane	25	1.35636	1.35625*	(35)
Benzene	25	1.50200	1.50197	(33)
Chlorobenzene	25	1.52611	1.52859*	(36)
Toluene	30	1.49526	1.49514	(33)
Methyl alcohol	20	1.32988	1.32981	(17)
Water	25	1.33398	1.33398	(37)

* Values of n_0 were obtained by interpolation.

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Table II. Least-squares fit for data on fringe shift as a function of pressure for liquids,
 $\lambda = 546.1 \text{ nm}$.

Liquid	Temp. (°C)	$f/t_0 = AP + BP^{1/2} + CP^{1/3} + DP^{1/4} + EP^{1/5}$					rms error of fit
		$A \times 10^{-2}$ ($\text{cm}^{-1}/\text{kbar}$)	$B \times 10^{-3}$ ($\text{cm}^{-1}/\text{kbar}^2$)	$C \times 10^{-4}$ ($\text{cm}^{-1}/\text{kbar}^3$)	$D \times 10^{-4}$ ($\text{cm}^{-1}/\text{kbar}^4$)	$E \times 10^{-4}$ ($\text{cm}^{-1}/\text{kbar}^5$)	
CCl_4	25	-13.26	25.89	-8.65	11.16	-4.82	0.43
n-Decane	25	-5.11	8.70	-1.78	1.59	-0.51	0.31
n-Nonane	25	-3.92	5.82	-0.55	-0.16	0.29	0.45
n-Octane	25	-4.98	7.85	-1.30	0.83	-0.14	0.84
n-Heptane	25	-1.68	-3.35	4.07	-7.24	3.66	1.45
n-Hexane	25	-1.64	-3.90	4.31	-7.52	3.76	1.52
n-Pentane	25	-0.92	-5.52	4.95	-8.30	4.08	0.58
Benzene	25	-4.49	10.66	-2.59	2.73	-1.02	0.55
Chlorobenzene	25	-4.75	10.99	-2.87	3.16	-1.23	1.07
Toluene	30	-3.12	4.69	0.18	-1.38	0.89	0.84
Methyl alcohol	20	-1.99	1.20	1.27	-2.74	1.47	0.87
Water	25	-3.67	10.54	-3.83	5.10	-2.25	0.43

Table III. Piezo-optic properties of liquids, $\lambda = 546.1$ nm.

Liquid	Temp. (°C)	n_0	Max. Pressure (kbar)	Total No. of Fringes Shifted	$\Delta n_{\max} = (n_{\max} - n_0)$	
					Bogardus	Adams-Gibson
CCl_4	25	1.45951	1.96	355	0.0632 ₃	0.0632 ₀
n-Decane	25	1.41138	3.23	404	0.0734 ₁	0.0733 ₅
n-Nonane	25	1.40499	5.85	561	0.1041 ₈	0.1040 ₄
n-Octane	25	1.39682	6.02	584	0.1081 ₆	0.1080 ₄
n-Heptane	25	1.38682	11.52	792	0.1520 ₁	0.1515 ₈
n-Hexane	25	1.37508	11.66	822	0.1572 ₇	0.1568 ₂
n-Pentane	25	1.35636	14.00	939	0.1825 ₀	0.1817 ₈
Benzene	25	1.50200	1.06	227	0.0403 ₀	0.0402 ₈
Chlorobenzene	25	1.52611	8.60	738	0.1401 ₉	0.1399 ₅
Toluene	30	1.49526	11.61	884	0.1706 ₇	0.1701 ₉
Methyl alcohol	20	1.32988	14.00	689	0.1387 ₃	0.1381 ₃
Water	25	1.33398	11.03	397	0.0832 ₇	0.0829 ₂

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Table IV. Comparison of our experimental results with the data in the literature.

Liquid	T (°C)	λ (nm)	Max. Pressure (bar)	Δn		
				Present Work	Literature	Reference
Benzene	25	589.3	868	0.0341	0.0340	(8)
"	25	589.3	666.1	0.0274	0.0273	(15)
Water	25	546.1	1519.9	0.0201	0.0188	(11)
"	25	589.3	1108.6	0.0145	0.0146	(15)
CCl ₄	25	589.3	1116.7	0.0406	0.0406	(15)

FIGURE CAPTIONS

- Figure.1. Variation of the refractive indices of CCl_4 and benzene, with pressure.
- Figure 2. Variation of the refractive indices of n-decane, n-nonane, and n-octane, with pressure.
- Figure 3. Variation of refractive indices of toluene, chlorobenzene, and water, with pressure.
- Figure 4. Variation of the refractive indices of n-heptane, n-hexane, n-pentane, and methyl alcohol, with pressure.

1.8

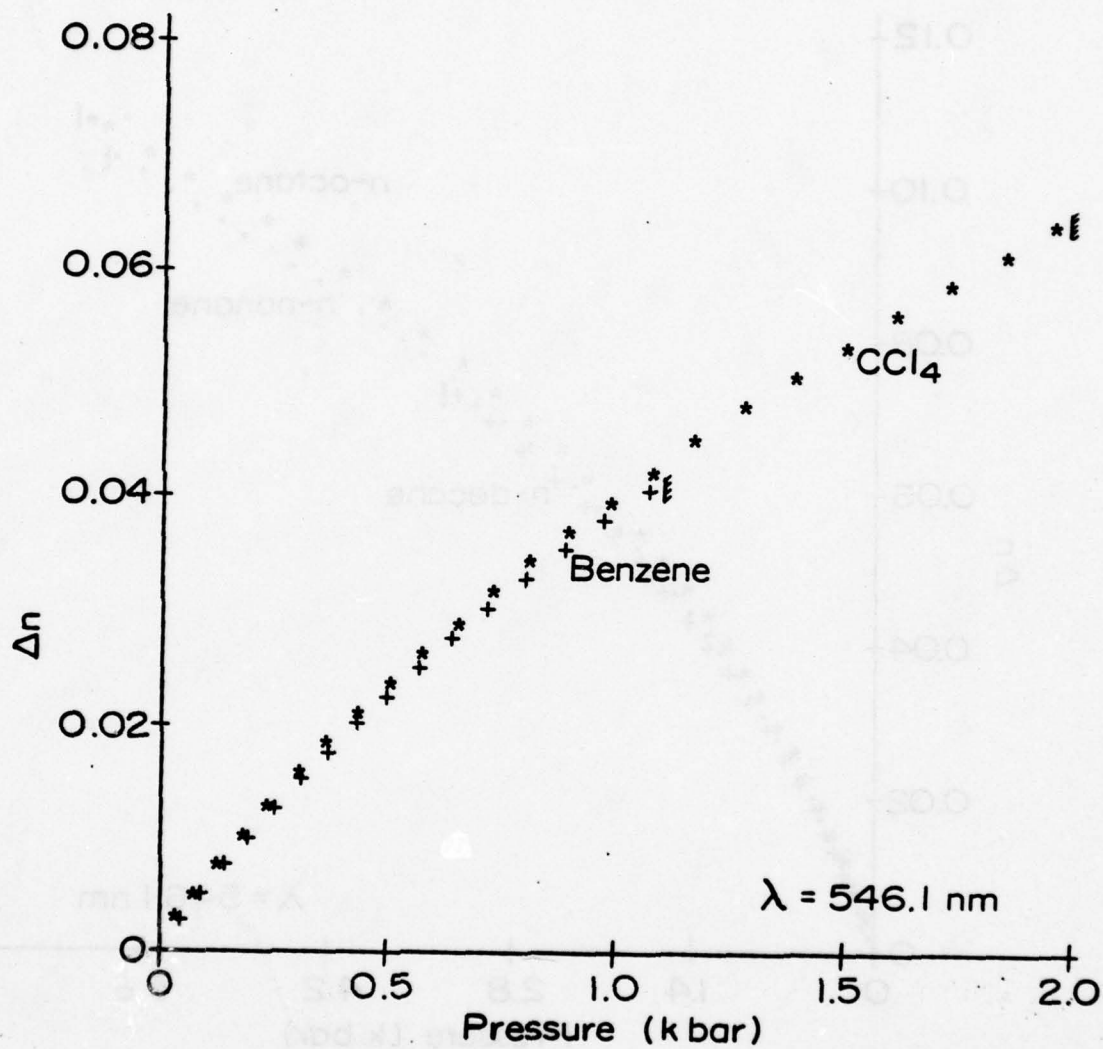


Figure.1. Variation of the refractive indices of CCl_4 and benzene, with pressure.

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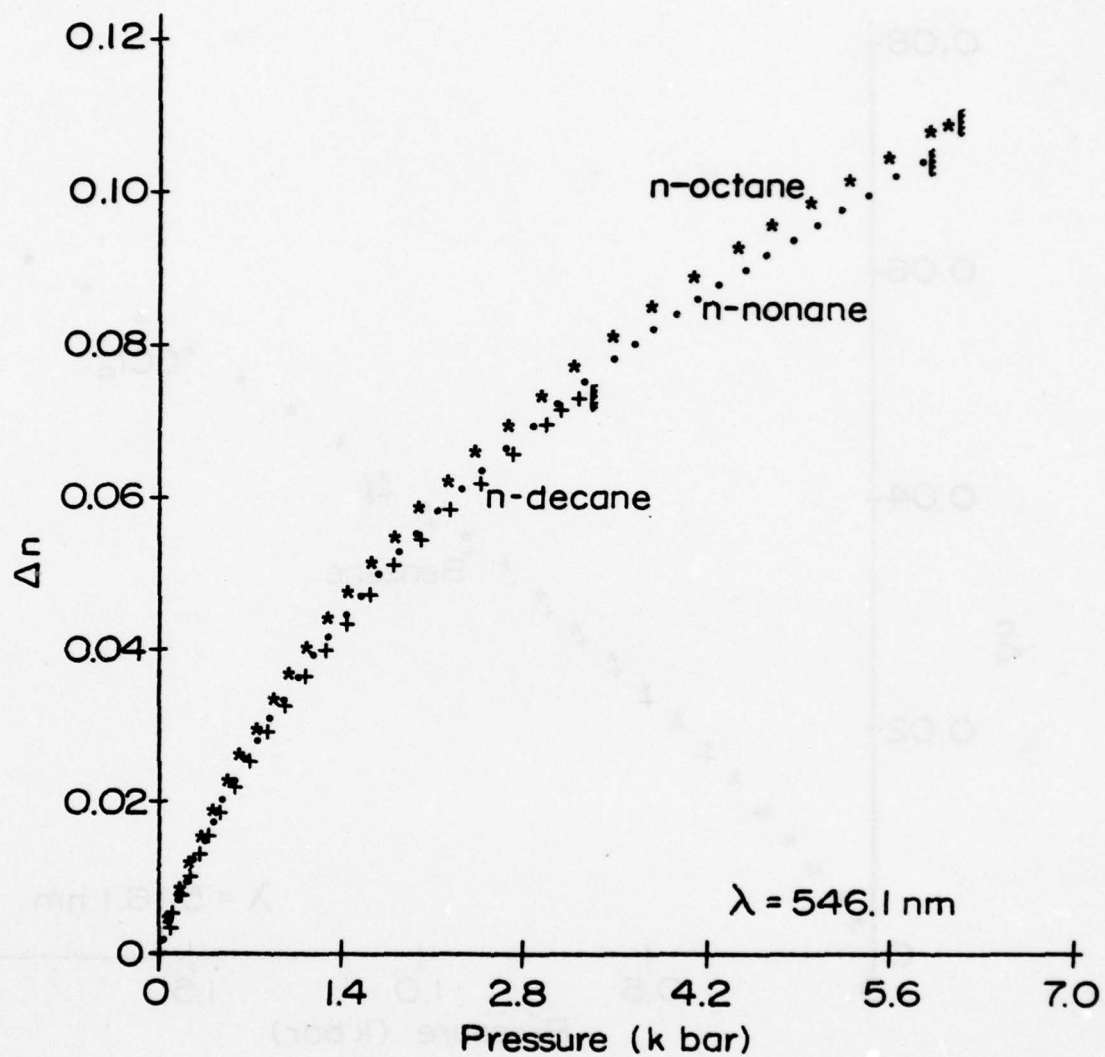


Figure 2. Variation of the refractive indices of n-decane, n-nonane, and n-octane, with pressure.

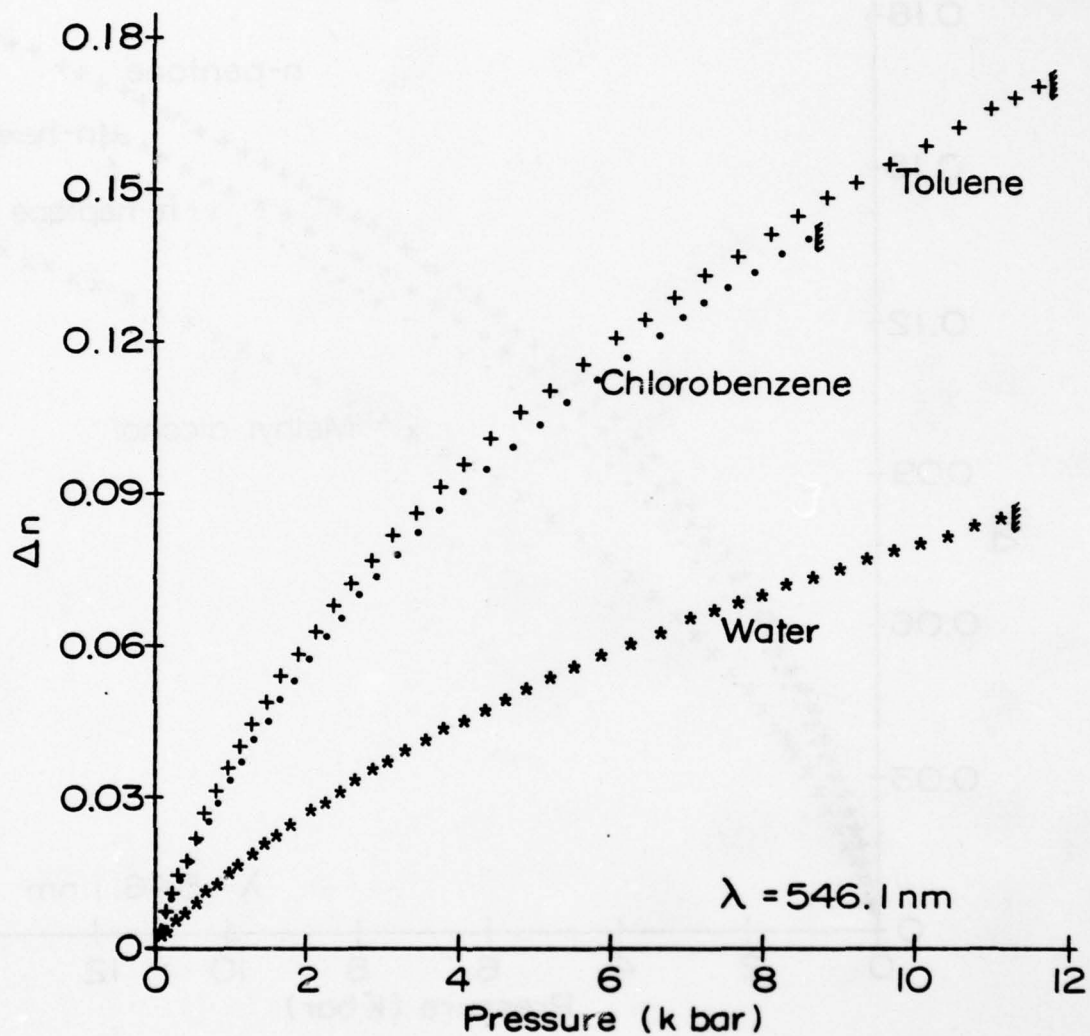


Figure 3. Variation of refractive indices of toluene, chlorobenzene, and water, with pressure.

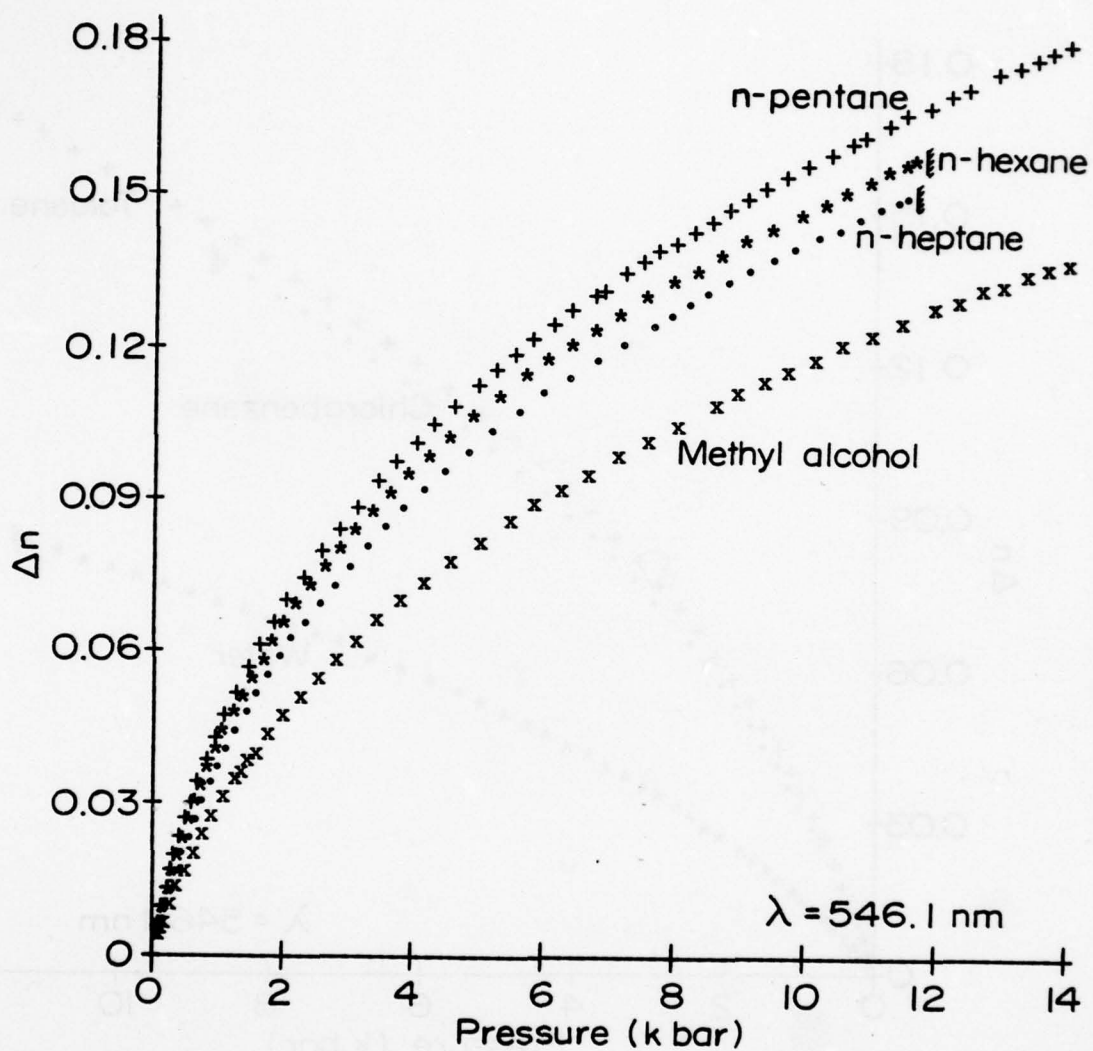


Figure 4. Variation of the refractive indices of n-heptane, n-hexane, n-pentane, and methyl alcohol, with pressure.

Piezo- and Elasto-Optical Properties of Liquids under High Pressure

II. Refractive Index vs. Strain*

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ABSTRACT

In paper I of this series it was reported that the refractive index of liquids increases with pressure with pronounced nonlinearity particularly at high pressures. This paper reports that this nonlinearity is reduced considerably when the same data on Δn is considered as a function of the volume strain indicating that the nonlinear piezo-optic behavior of liquids is just a manifestation of nonlinear P-V relationship. Further it is found that the slight nonlinearity noticed in $\Delta n - \Delta V/V_0$ relationship could be still further reduced when the variation in refractive index is treated as functions of the Lagrangian and Eulerian strains. In particular, the Eulerian strain ϵ is found to yield a much larger range of strain over which a simple linear relationship between Δn and ϵ is obtained irrespective of the nature of the liquid or the equation of state used to compute the strain.

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I. Introduction

Recently the authors⁽¹⁾ have been able to carry out precision interferometric measurements on a number of liquids at high pressures to 14 kbars. The liquids studied were composed of molecules of widely varying size, shape and symmetry. In every case it was found that the refractive index increases with pressure with pronounced nonlinearity. In the case of solids, such as alkali halides⁽²⁾, α -quartz⁽³⁾, and vitreous silica⁽⁴⁾, etc., where also such high pressure interferometric measurements have been carried out it was found that the relationship between Δn and pressure becomes slightly nonlinear at pressure above 5 kbars, but the same data exhibit perfect linear relationship between Δn and the volume strain $\frac{\Delta V}{V_0}$ in the entire range of pressures studied, provided the latter quantities are evaluated with the help of nonlinear theory of elasticity. The maximum volume strain involved in the case of solids was about 9% and since the volume strain is related to η by the relation $\frac{\Delta V}{V_0} = 3\eta + \frac{3}{2}\eta^2 + \dots \approx 3\eta$, one may expect the perfect linear relationship between Δn and η as well as Δn and $\frac{\Delta V}{V_0}$. Since such a linear relationship is found to be valid in such high-band-gap inorganic solids where there is considerable amount of overlap of the electronic wave functions of neighboring ions, one can expect a similar linear Δn vs η relationship in the case of liquids as well, where there is usually a sufficient free volume such that under compression the average molecular packing is increased without significantly affecting the interaction between neighboring molecules.

However, the results of piezo-optic measurements at high pressures on a number of liquids reveal, as will be shown in this article, that at low pressures where η is small, Δn vs η is exactly linear, but the relationship becomes nonlinear at high pressures. Such a nonlinearity can arise from one or more of the following causes: (i) unreliable P-V data used to evaluate η , (ii) instead of Lagrangian strain η , the Eulerian strain or some other representation of strain should be used, (iii) use of an inappropriate equation of state for the liquids when extrapolating and interpolating literature P-V data to cover the entire pressure range investigated, and (iv) intrinsic nonlinearity of Δn with respect to all strain measures for liquids. Investigation into these possibilities has been carried out with the help of the high pressure piezo-optic data on a number of liquids reported earlier, and the results and the conclusions are presented in this and the following article.

But before describing the results, a brief discussion on the proper description of various strains is given below, since on reference to the literature it is found that there is a considerable amount of confusion in the definition, nomenclature, and the various symbols employed in the description of the strains and their properties.

II. Finite Strain

In what follows we shall adopt in general the notation employed by Truesdell and Toupin⁽⁵⁾ in their classic treatise on continuum mechanics, with a few exceptions such as, for the Lagrangian and Eulerian strains we shall use the notation commonly used by high

pressure physicists⁽⁶⁻¹²⁾. Rectangular Cartesian coordinate system will be used for the description of the initial and final configurations of a deformable body.

Let the coordinates of a particle in the initial or unstrained state of the body be (a_1, a_2, a_3) , and in the final or strained state be (x_1, x_2, x_3) . Thus the deformation of the body is known if x_1, x_2, x_3 are known functions of a_1, a_2, a_3 ; i.e.,

$$x_i = x_i(a_1, a_2, a_3) \quad (1)$$

This is a transformation from a_1, a_2, a_3 to x_1, x_2, x_3 . The unstrained coordinates a_i which identify the particles are called materials coordinates. A description which like Eqn. (1) uses a_i as independent variables is called a material description. Instead if one uses x_i as independent variables, as

$$a_i = a_i(x_1, x_2, x_3) \quad (2)$$

then such a description is called spatial description.

Consider an infinitesimal line element connecting a particle P (a_1, a_2, a_3) to a neighboring particle P' $(a_1 + da_1, a_2 + da_2, a_3 + da_3)$. The square of the length ds_a of PP' in the initial configuration is given by

$$ds_a^2 = da_1^2 + da_2^2 + da_3^2 = \delta_{ij} da_i da_j \quad (3)$$

When P and P' are deformed to the points Q (x_1, x_2, x_3) and Q' $(x_1 + dx_1, x_2 + dx_2, x_3 + dx_3)$ respectively, the square of length ds_x of the element QQ' in the final configuration is

$$ds_x^2 = dx_1^2 + dx_2^2 + dx_3^2 = \delta_{ij} dx_i dx_j \quad (4)$$

The difference between the squares of the lengths may be written, either as

$$ds_x^2 - ds_a^2 = \left(\frac{\partial x_i}{\partial a_j} \frac{\partial x_i}{\partial a_k} - \delta_{jk} \right) da_j da_k \quad (5)$$

or as

$$ds_x^2 - ds_a^2 = \left(\delta_{jk} - \frac{\partial a_i}{\partial x_j} \frac{\partial a_i}{\partial x_k} \right) dx_j dx_k \quad (6)$$

We define the strain components

$$\eta_{jk} = \frac{1}{2} \left(\frac{\partial x_i}{\partial a_j} \frac{\partial x_i}{\partial a_k} - \delta_{jk} \right) \quad (7)$$

and

$$\epsilon_{jk} = \frac{1}{2} \left(\delta_{jk} - \frac{\partial a_i}{\partial x_j} \frac{\partial a_i}{\partial x_k} \right) \quad (8)$$

Thus, η_{ij} and ϵ_{ij} are strain components in the coordinate system a_i (materials coordinates) and x_j (spatial coordinates), respectively. In Truesdel and Toupin's notation⁽⁵⁾ η_{ij} and ϵ_{ij} are denoted by E_{ij} and e_{ij} , respectively. Truesdell and Toupin call the two sets of quantities $\frac{\partial x_i}{\partial a_j}$ and $\frac{\partial a_i}{\partial x_j}$ deformation gradients in the material and spatial descriptions, respectively. Define the deformation gradient, \vec{F} (13) by

$$\vec{F} = \vec{\nabla}_a x; \quad F_{ij} = \frac{\partial x_i}{\partial a_j}. \quad (9)$$

\vec{F} is assumed to have an inverse, which will be denoted by \vec{G} : $\vec{G} = \vec{F}^{-1}$.

By the polar decomposition theorem⁽¹⁴⁾, \vec{F} has two unique multiplicative decompositions

$$\vec{F} = \vec{R} \vec{U}, \quad \vec{F} = \vec{V} \vec{R} \quad (10)$$

in which \vec{R} is orthogonal, and \vec{U} and \vec{V} are symmetric and positive

definite. These are called, by Truesdell and Noll, the rotation tensor, and the right and left stretch tensors, respectively. Then the right and left Cauchy-Green tensors can be defined by

$$\vec{C} = \vec{U}^2 = \vec{F}^T \vec{F}, \quad \vec{B} = \vec{V}^2 = \vec{F} \vec{F}^T = \vec{R} \vec{C} \vec{R}^T \quad (11)$$

Another strain tensor will now be defined

$$\vec{c} = \vec{B}^{-1} = \vec{G}^T \vec{G} \quad (12)$$

\vec{c} is called the Cauchy deformation tensor⁽¹⁵⁾. Components of \vec{C} and \vec{c} are, respectively,

$$C_{ij} = (F^T F)_{ij} = F_{ki} F_{kj} = \frac{\partial x_k}{\partial a_i} \frac{\partial x_k}{\partial a_j} \quad (13)$$

and

$$c_{ij} = (G^T G)_{ij} = G_{ki} G_{kj} = \frac{\partial a_k}{\partial x_i} \frac{\partial a_k}{\partial x_j} \quad (14)$$

Now we can write the strain components η_{ij} and ϵ_{ij} in terms of \vec{C} and \vec{c} , respectively as

$$\eta_{ij} = \frac{1}{2} \left(\frac{\partial x_k}{\partial a_i} \frac{\partial x_k}{\partial a_j} - \delta_{ij} \right) = \frac{1}{2} (C_{ij} - \delta_{ij}) \quad (15)$$

and

$$\epsilon_{ij} = \frac{1}{2} \left(\delta_{ij} - \frac{\partial a_k}{\partial x_i} \frac{\partial a_k}{\partial x_j} \right) = \frac{1}{2} (\delta_{ij} - c_{ij}). \quad (16)$$

Hence

$$\vec{\eta} = \frac{1}{2} (\vec{C} - 1) \quad (17)$$

and

$$\vec{\epsilon} = \frac{1}{2} (1 - \vec{c}). \quad (18)$$

According to Truesdell and Toupin⁽¹⁶⁾ $\vec{\eta}$ and $\vec{\epsilon}$ are called the Green-St. Venant strain tensor and Almansi-Hamel strain tensor, respectively. But amongst the high pressure experimentalists the commonly used terminology for $\vec{\eta}$ and $\vec{\epsilon}$ are the Lagrangian and Eulerian strain tensors, respectively.

Davies⁽¹⁷⁾ has recently defined another set of strain tensors, \vec{b} , \vec{D} and \vec{E} analogous to the Cauchy deformation tensor \vec{c} , Lagrangian strain tensor $\vec{\eta}$ and the Eulerian strain tensor $\vec{\epsilon}$, respectively. The strain tensors \vec{C} , \vec{c} , $\vec{\eta}$, and $\vec{\epsilon}$ and their analogues can be written in parallel as the following:

$$\vec{C} = \vec{U}^2 = \vec{F}^T \vec{F} \quad ; \quad \vec{B} = \vec{V}^2 = \vec{F} \vec{F}^T \quad (19)$$

$$\vec{b} = \vec{C}^{-1} = \vec{G} \vec{G}^T \quad ; \quad \vec{c} = \vec{B}^{-1} = \vec{G}^T \vec{G} \quad (20)$$

$$\vec{\eta} = \frac{1}{2} (\vec{C} - 1) \quad ; \quad \vec{D} = \frac{1}{2} (\vec{B} - 1) \quad (21)$$

$$\vec{E} = \frac{1}{2} (1 - \vec{b}) \quad ; \quad \vec{\epsilon} = \frac{1}{2} (1 - \vec{c}) . \quad (22)$$

At this point it is important to point out that Davies⁽¹⁷⁾ in his first article has denoted the Cauchy deformation tensor \vec{c} and its analogue \vec{b} by \vec{b} and \vec{c} , respectively. Further, \vec{E} and $\vec{\epsilon}$ have been denoted by Davies⁽¹⁷⁾ as \vec{e} and \vec{d} , respectively, whereas Thomsen⁽¹⁰⁾ denotes \vec{E} by \vec{E} .

It is seen that the strain tensors on the left column of Eqns. (19-22) are functions of \vec{U} and are referred to the initial or undeformed state, whereas those on the right column are functions of \vec{V} and are referred to the final or deformed state. It is required, by the principles of classical physics, that all constitutive equations must be invariant⁽¹⁸⁾ under changes of frame of reference. The principle of frame-indifference (or invariance) of material properties has been fully discussed by Truesdell and Noll⁽¹⁹⁾ and a useful review on the frame-indifference requirements for strain tensors is also given by Davies⁽¹⁷⁾. It has been shown that any strain tensor which depends on \vec{U} is frame-indifferent; conversely one that depends on \vec{V} is not

frame-indifferent. Therefore, all the strains defined on the left column of Eqns. (19-22) are frame-indifferent, whereas those on the right are not.

By the principle of frame-indifference, the strain tensors can be classified into two classes: material strain tensors which are invariant under changes of frame of reference and spatial strain tensors which are not. The Lagrangian strain tensor $\vec{\eta}$ is an example of a material strain tensor, and the Eulerian strain tensor, $\vec{\epsilon}$, is an example of a spatial strain tensor. The use of the non-frame-indifferent Eulerian strain tensor $\vec{\epsilon}$ by earlier workers^(7, 20-21) has not usually led to errors because of the special situations considered by them, such as the case of isotropic material under hydrostatic pressure. Davies⁽¹¹⁾ has emphasized that the frame-indifferent analogue $\vec{\bar{\epsilon}}$ of the Eulerian strain $\vec{\epsilon}$ should in general be used rather than $\vec{\epsilon}$. However, for the special case of isotropic material under hydrostatic pressure Truesdell and Toupin⁽²²⁾ have shown that $\vec{\bar{\epsilon}} \equiv \vec{\epsilon}$ and thus the invariance condition is trivially satisfied.

Hence for the problem of interest in our case, i.e., for liquids under hydrostatic pressure, $\vec{\bar{\epsilon}} \equiv \vec{\epsilon}$ and it is seen from Eqns. (21) and (22) that

$$(1 + 2\vec{\eta}) = (1 - 2\vec{\bar{\epsilon}})^{-1} = (1 - 2\vec{\epsilon})^{-1}. \quad (23)$$

In terms of specific volume, for the case of isotropic strains, the Lagrangian strain η is given by

$$\eta = \frac{1}{2} \left[\left(\frac{V}{V_0} \right)^{2/3} - 1 \right] \quad (24)$$

and the Eulerian strain ϵ by

$$E \equiv \epsilon = \frac{1}{2} \left[1 - \left(\frac{V}{V_0} \right)^{2/3} \right]. \quad (25)$$

On the other hand, Eqns. (23) and (24) can be written in terms of the volume strain $\Delta V/V_0$ as

$$\frac{\Delta V}{V_0} = (1 + 2\eta)^{3/2} - 1 \quad (26)$$

$$\text{and} \quad \frac{\Delta V}{V_0} = (1 - 2\epsilon)^{-3/2} - 1, \quad (27)$$

$$\text{where} \quad \frac{\Delta V}{V_0} = \frac{V - V_0}{V_0}.$$

To third order, the power series expansion of Eqns. (26) and (27) are, respectively,

$$\frac{\Delta V}{V_0} = 3\eta + \frac{3}{2}\eta^2 - \frac{3}{4}\eta^3 + \dots \quad (28)$$

$$\text{and} \quad \frac{\Delta V}{V_0} = 3\epsilon + \frac{15}{2}\epsilon^2 - \frac{15}{4}\epsilon^3 + \dots \quad (29)$$

III. Results and Discussion

As mentioned in the last article, precision interferometric measurements on a number of liquids at high pressures reveal that the refractive index increases with pressure with pronounced nonlinearity in every case. The present studies reveal that the major cause for this nonlinearity is the nonlinear stress-strain relationship. For example, Fig. 1 shows a representative graph of the variation of refractive index Δn with volume strain for the case of water. Gibson and Loeffler's P-V data⁽²³⁾ on water and the Tait's equation⁽²⁴⁾ of

state were used along with Δn vs P data discussed in the earlier article, to arrive at Fig. 1. Even though it is not shown here the Δn vs $\Delta V/V_0$ curve for water is essentially the same when Bridgman's P - V data is used instead of Gibson and Loeffler's data, or when any of the various equations of state prevalent in the literature is used instead of the Tait's equation. Exactly similar statements can be made with regard to the variation of refractive index of all the other liquids as well, which have been studied thus far. In every case the grossly nonlinear behavior observed in Δn vs P relationship is considerably reduced when the same data on Δn are considered as a function of the volume strain. Further, it is found that the sublinear Δn vs P relationship becomes a superlinear Δn vs $\Delta V/V_0$ dependence.

From Eqns. (28) and (29) it is seen that the volume strain $\Delta V/V_0$ itself is nonlinearly related to the Lagrangian and Eulerian strains. Hence, the dependence of Δn on these two strains were next considered for all the above liquids. Figs. 2-7 show representative results obtained on one liquid--water; the results for the other liquids are again very similar and hence are not presented. Bridgman's early P - V data⁽²⁵⁾ on water were used to calculate the volume strain; and for computation in between the P - V data points the Tait, first-order Murnaghan⁽²⁶⁾ and Keane⁽²⁷⁾ equations of state were used in Figs. 2-4 respectively. Figs. 5-7 represent similar set of curves for water except that the Bridgman's later P - V data⁽²⁸⁾ were used in these cases. In all these figures the change in refractive index of water is plotted both as a function of the Lagrangian strain η and the Eulerian strain ϵ .

It is seen that in every case the nonlinearity is much smaller than that in Fig. 1. and that the Eulerian representation yields in every case a much larger range of strain over which linear relationship appears to hold good. Comparison of Figs. 2-4 with 5-7 reveal that the use of more accurate P-V data extends the linear $\Delta n - \epsilon$ dependence range of strain. In other words, irrespective of the source of P-V data used to compute the strains, the Eulerian strain appears to yield a larger range of linear relationship with Δn . Here it must be pointed out that exactly similar results were obtained when the piezo-optic data on water were analyzed using the other equations of state, such as the first- and second-order Birch Equations⁽²⁹⁾, second-order Murnaghan equation⁽²⁹⁾ and the Linear Secant-Modulus equation⁽³⁰⁾. Again, these conclusions are found to be true in every liquid studied thus far, namely - liquids of long chain molecules (n-alkanes), planar molecules (benzene and chlorobenzene), nearly spherical molecules (carbon tetrachloride), polar (water, methyl alcohol) and nonpolar molecules.

Thus in summary, we can state that the Eulerian representation yields a much larger range of strain over which a simple linear relationship between Δn and ϵ is obtained irrespective of (i) the nature of the liquid (ii) the equation of state used to compute the strain and (iii) even the source of the P-V data.

From this one might be tempted to conclude the Eulerian strain is a more useful strain measure than the Lagrangian strain. But such a conclusion would be erroneous as has been pointed out by Birch⁽⁷⁾ and Truesdell and Toupin⁽²²⁾, for a particular problem a particular choice of strain measure may be helpful in yielding a simple mathematical

expression and that a generalization from any one such example is not warranted. In other words, it is just a matter of convenience to choose an appropriate frame of reference so that the results can be expressed by simple compact expressions.

Birch further has analyzed all the published data on compressibility and its variation with pressure on a large number of elements as well as inorganic compounds and finds that the use of Eulerian representation of the strain does indeed yield a simple relation to express the elastic behavior of these solids, even though the density is more than doubled in many instances. The present studies reveal that the elasto-optic behavior of liquids can also be expressed by a simple linear relation between Δn and the strain, if the Eulerian frame of reference is employed to evaluate the strain.

The elasto-optic coefficient $\rho(dn/dp)$ is given by

$$\rho \left[\frac{dn}{dp} \right] = - \Delta n / (\Delta V / V_0). \quad (30)$$

From Fig. 1 it is seen that the slope of the curve between Δn and the volume strain is not constant. Hence $\rho(dn/dp)$ is also not constant over the entire stability range of the liquid. In the case of solids⁽²⁻⁴⁾ it may be recalled that $\rho(dn/dp)$ was found to be constant over the range of pressures employed. But solids being relatively incompressible the total volume strains involved never exceeded 9%, whereas in the case of liquids the corresponding values of volume strain are as large as 33%. Consequently it is not surprising to find that $\rho(dn/dp)$ is not constant in the case of liquids where the strains are much larger than 9%. Hence in further discussions of the piezo-optic behavior of liquids, we will deal mainly with the variation of Δn with density rather than the behavior of $\rho(dn/dp)$, and this is presented in paper III of this series.

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Figure Captions

- Figure 1. Variation of refractive index of water with volume strain.
- Figure 2. Variation of refractive index of water with η , the Lagrangian strain and ϵ , the Eulerian strain. Strains computed with the help of Tait's Equation⁽²⁴⁾ using Bridgman's earlier P-V data⁽²⁵⁾.
- Figure 3. Variation of refractive index of water with η , the Lagrangian strain and ϵ , the Eulerian strain. Strains computed with the help of first-order Murnaghan Equation⁽²⁶⁾ using Bridgman's earlier P-V data⁽²⁵⁾.
- Figure 4. Variation of refractive index of water with η , the Lagrangian strain and ϵ , the Eulerian strain. Strains computed with the help of Keane's Equation⁽²⁷⁾ using Bridgman's earlier P-V data⁽²⁵⁾.
- Figure 5. Variation of refractive index of water with η , the Lagrangian strain and ϵ , the Eulerian strain. Strains computed with the help of Tait's Equation⁽²⁴⁾ using Bridgman's later P-V data⁽²⁸⁾.
- Figure 6. Variation of refractive index of water with η , the Lagrangian strain and ϵ , the Eulerian strain. Strains computed with the help of first-order Murnaghan's Equation⁽²⁶⁾ using Bridgman's later P-V data⁽²⁸⁾.
- Figure 7. Variation of refractive index of water with η , the Lagrangian strain and ϵ , the Eulerian strain. Strains computed with the help of Keane's Equation⁽²⁷⁾ using Bridgman's later P-V data⁽²⁸⁾.
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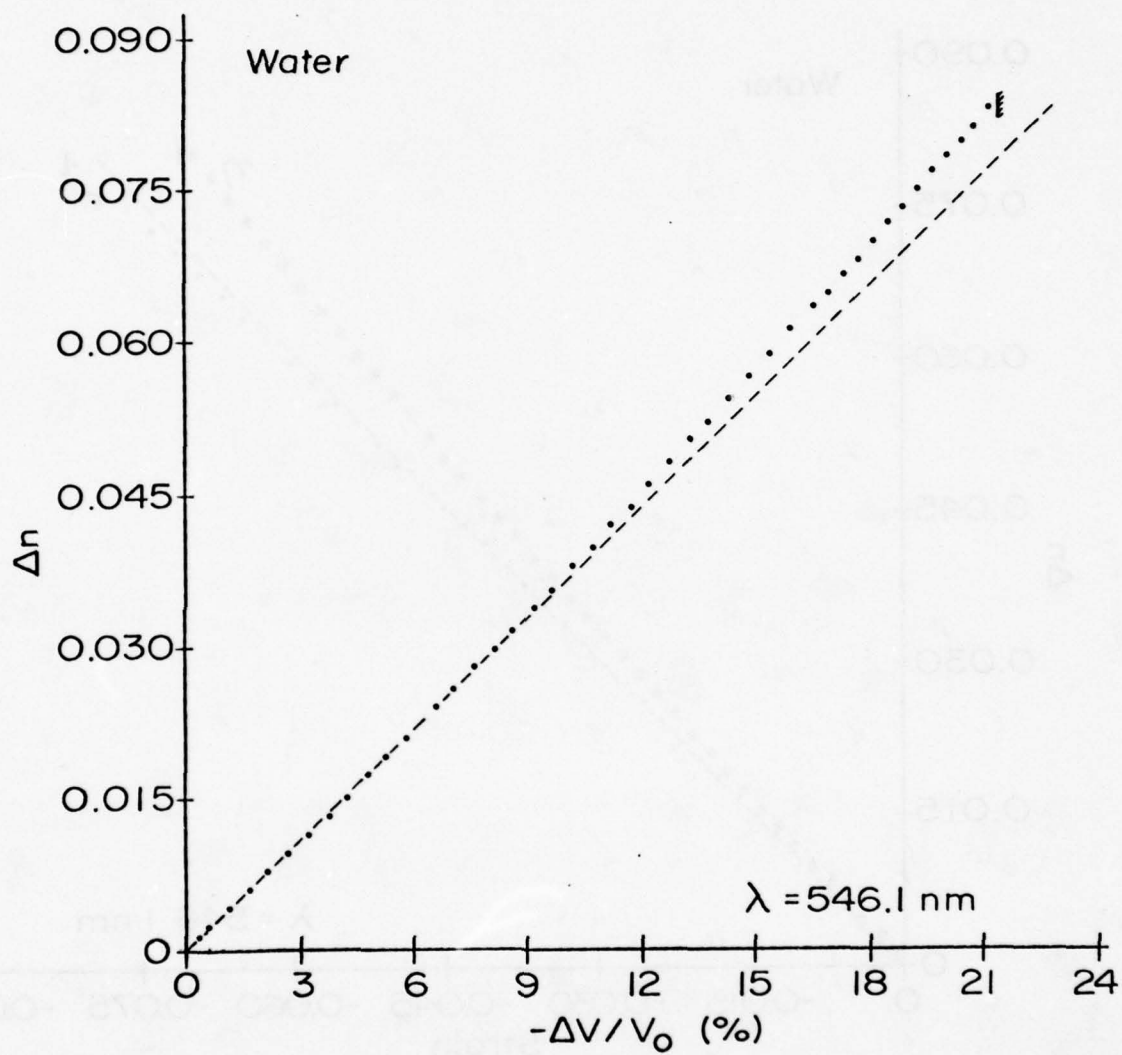


Figure 1. Variation of refractive index of water with volume strain.

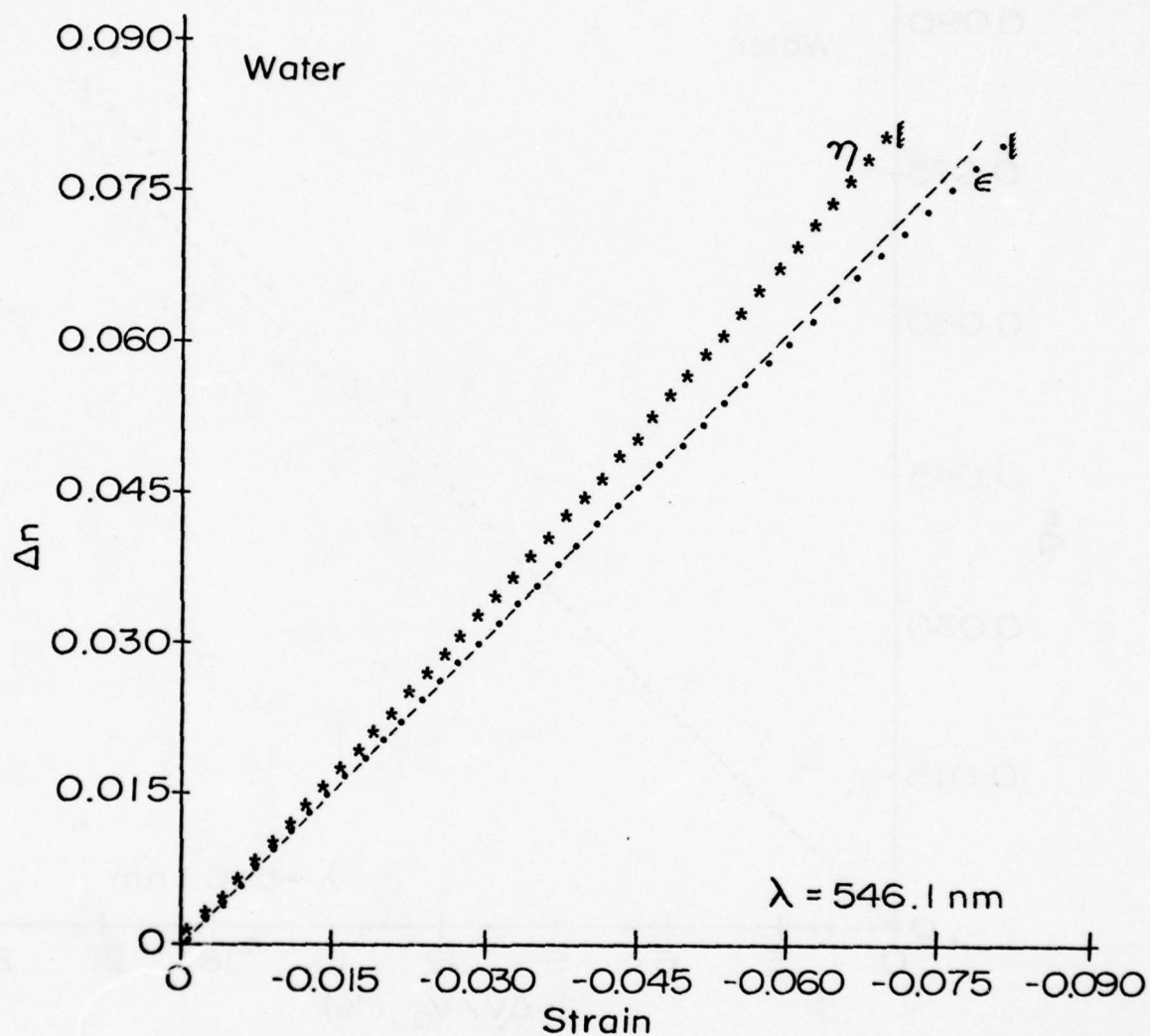


Figure 2. Variation of refractive index of water with η , the Lagrangian strain and ϵ , the Eulerian strain. Strains computed with the help of Tait's Equation⁽²⁴⁾ using Bridgman's earlier P-V data⁽²⁵⁾.

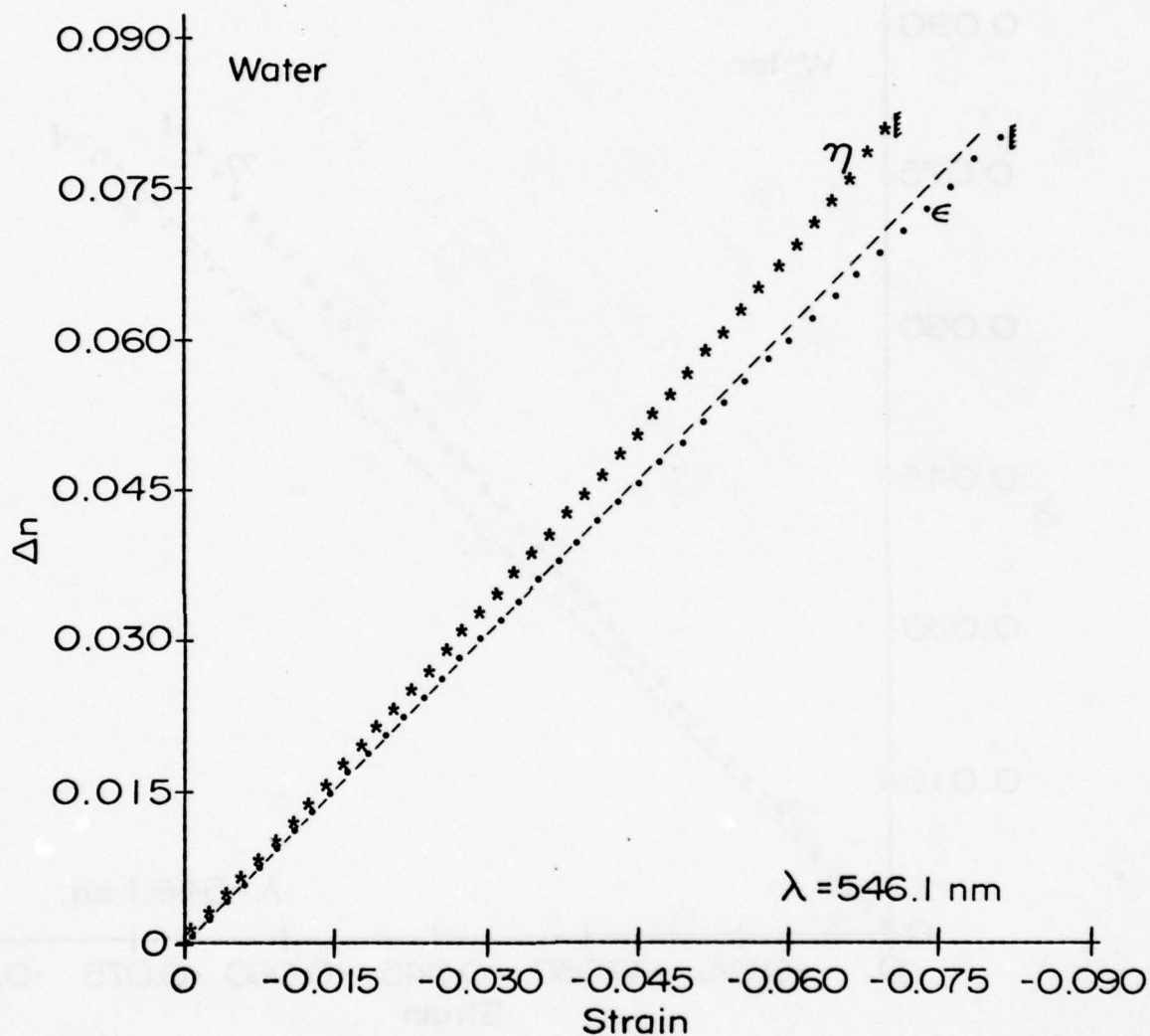


Figure 3. Variation of refractive index of water with η , the Lagrangian strain and ϵ , the Eulerian strain. Strains computed with the help of first-order Murnaghan Equation(26) using Bridgman's earlier P-V data(25).

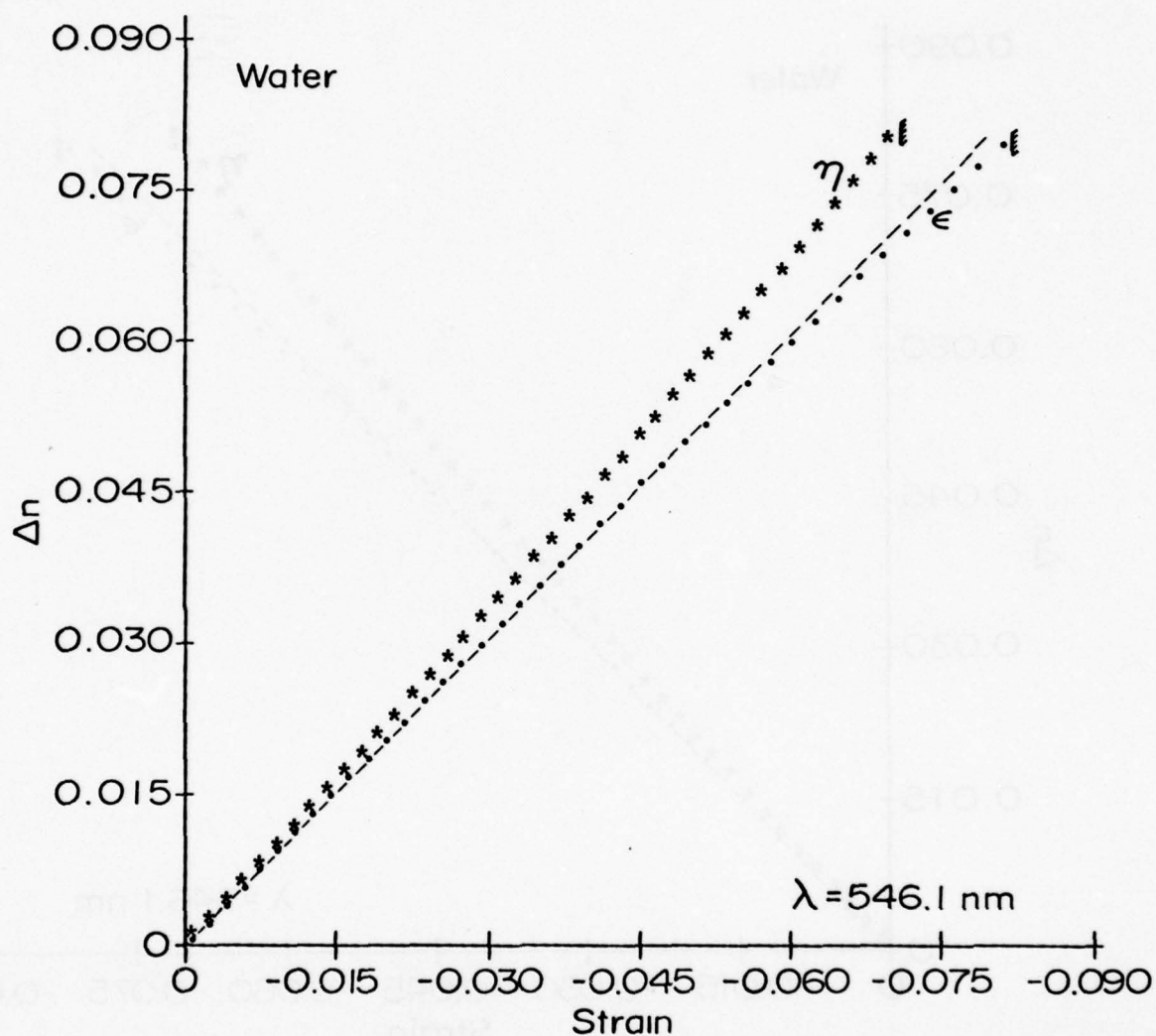


Figure 4. Variation of refractive index of water with η , the Lagrangian strain and ϵ , the Eulerian strain. Strains computed with the help of Keane's Equation⁽²⁷⁾ using Bridgman's earlier P-V data⁽²⁵⁾.

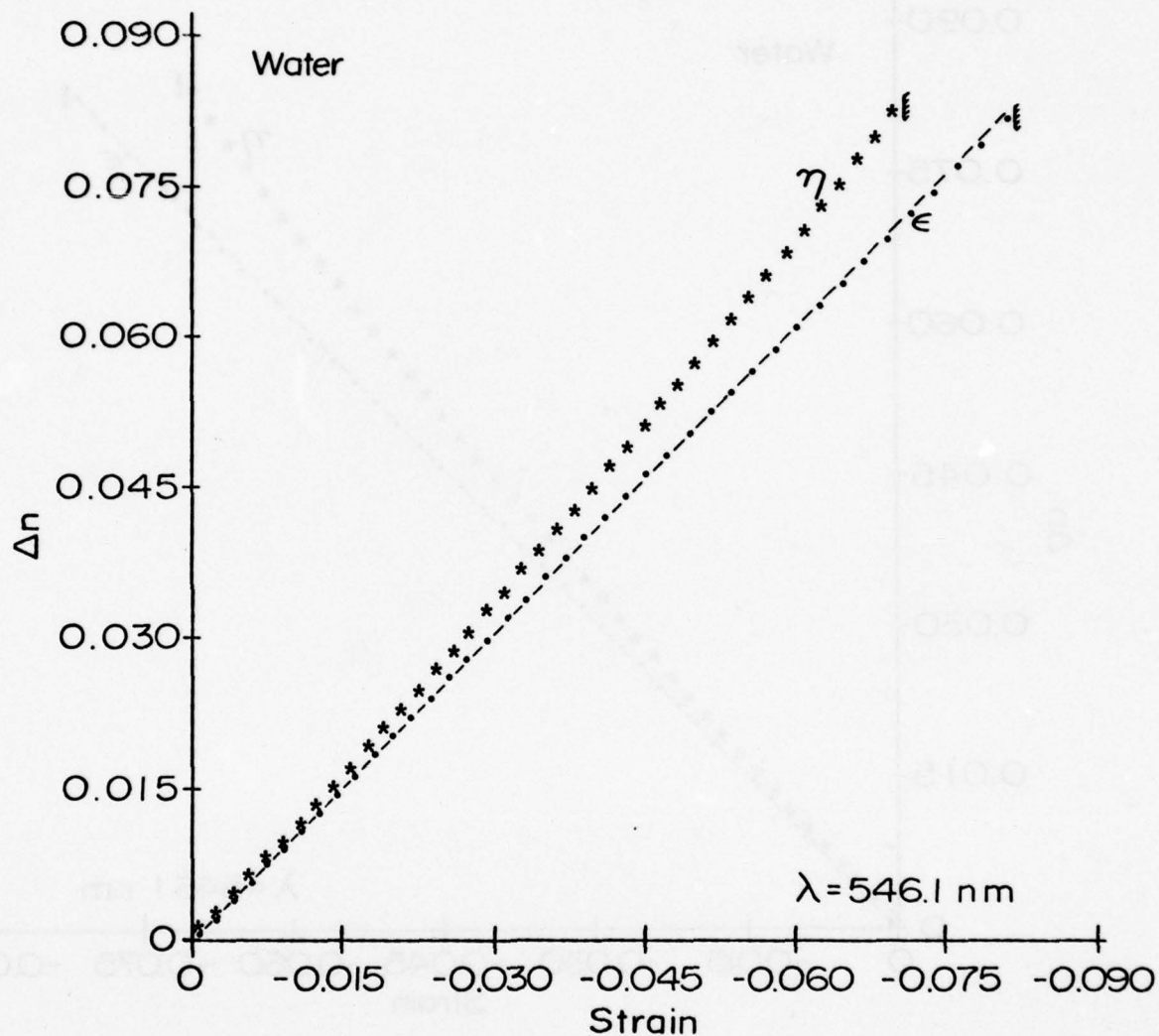


Figure 5. Variation of refractive index of water with η , the Lagrangian strain and ϵ , the Eulerian strain. Strains computed with the help of Tait's Equation⁽²⁴⁾ using Bridgman's later P-V data⁽²⁸⁾.

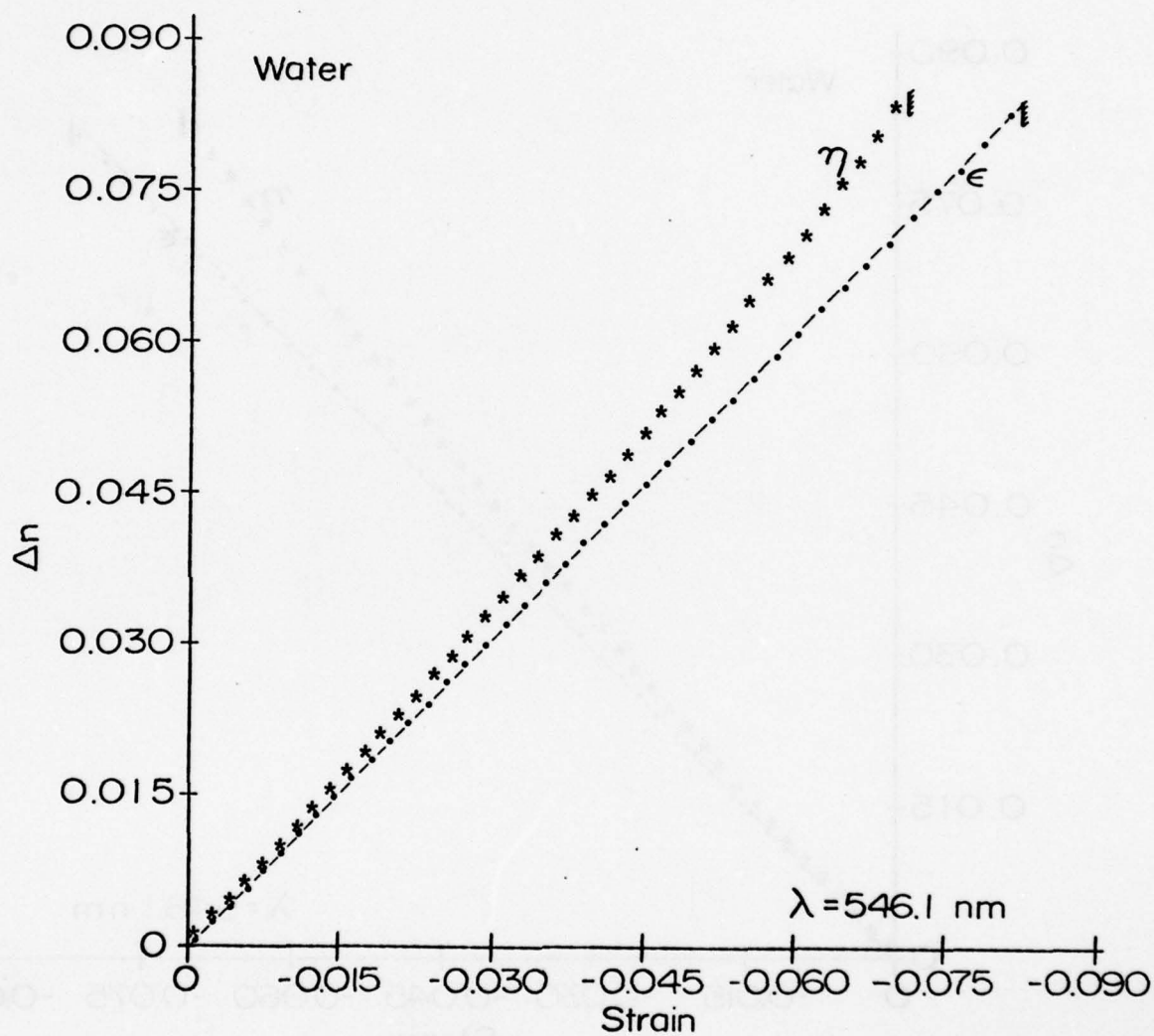


Figure 6. Variation of refractive index of water with η , the Lagrangian strain and ϵ , the Eulerian strain. Strains computed with the help of first-order Murnaghan's Equation⁽²⁶⁾ using Bridgman's later P-V data⁽²⁸⁾.

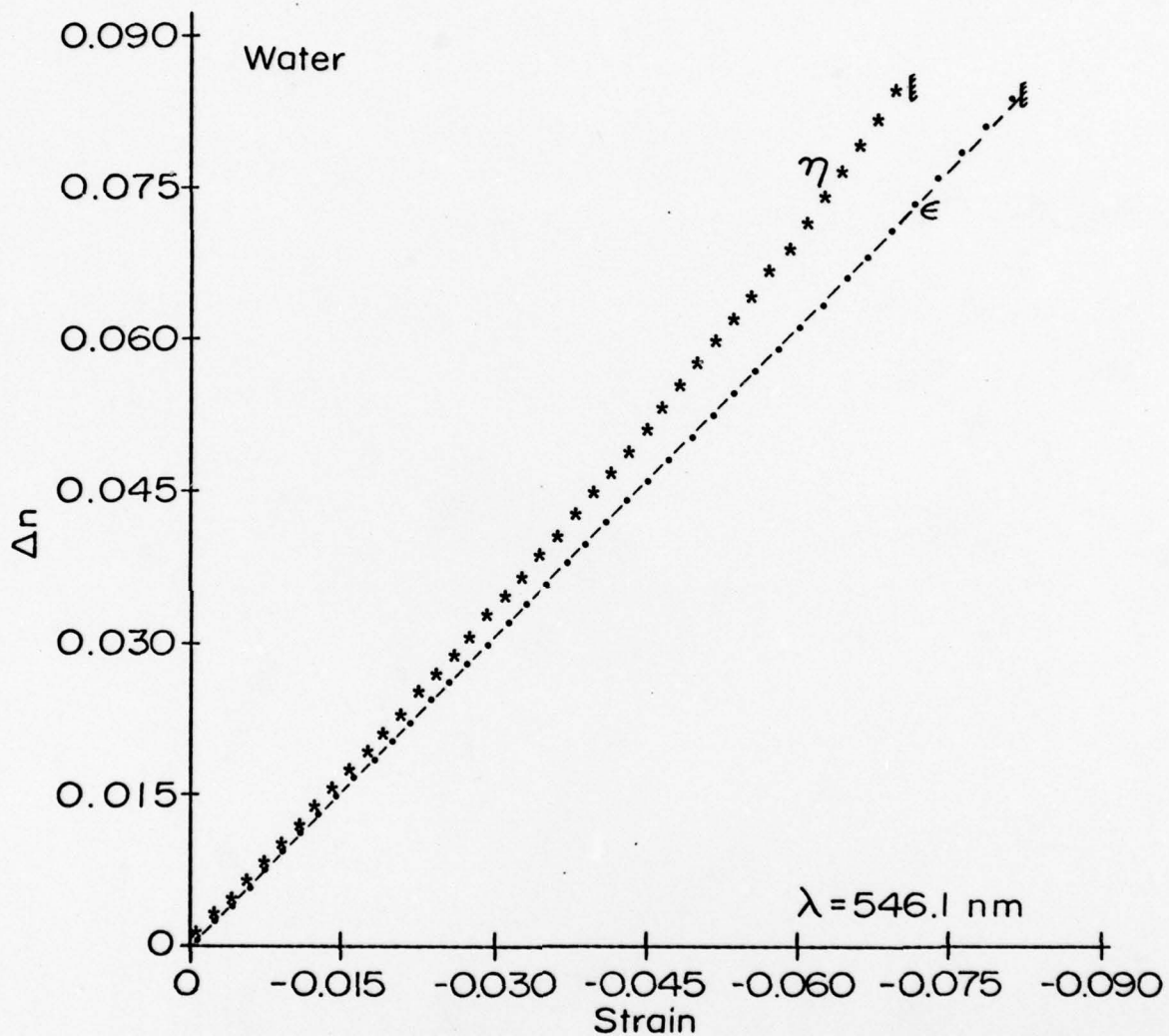


Figure 7. Variation of refractive index of water with η , the Lagrangian strain and ϵ , the Eulerian strain. Strains computed with the help of Keane's Equation⁽²⁷⁾ using Bridgman's later P-V data⁽²⁸⁾.

PIEZO-OPTIC BEHAVIOR AND THE EQUATION OF STATE OF LIQUIDS*

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INTRODUCTION

Consider the piezo-optic behavior of materials in their transparent region of spectrum. In the case of solids such as alkali-halides^[1], α -quartz^[2], vitreous silica^[3], etc., the relationship between the change in refractive index Δn and pressure becomes slightly nonlinear at high pressures (say above 5 kbars), but the same data exhibit perfect linear relationship between Δn and the Lagrangian strain η in the entire range of pressures studied. In the case of liquids such as water and CCl_4 , as mentioned in a previous article^[4], Δn is grossly nonlinear with pressure, and Δn vs η is linear only at strains less than 2 or 3%. Motivated by the linearity of Δn vs η for the solids, one can view the nonlinearity of the Δn vs η for the liquids as possibly caused by (i) unreliable P-V data used to evaluate η , (ii) use of an inappropriate equation of state for the liquids when extrapolating and interpolating literature P-V data to cover our entire 14 kbar pressure range, (iii) nonapplicability of Lagrangian strain as a strain measure at our very high strains and (iv) perhaps intrinsic nonlinearity of Δn with respect to all strain measures for liquids. Investigation into these possibilities was made with high pressure interferometric measurements on a number of liquids under hydrostatic pressure and the results and conclusions are presented here.

* To be published in Proc. 6th AIRAPT International High Pressure Conf., Boulder, Colorado (1977).

DEFINITION OF VARIOUS STRAINS

Thomsen^[5] and Davies^[6,7] have recently reviewed the significance and properties of the various representation of strains, in particular the Lagrangian (η) and the Eulerian strain (ϵ). In brief, for the case of liquids under hydrostatic pressure, we have

$$\eta = \frac{1}{2} \left| \left(\frac{V}{V_0} \right)^{2/3} - 1 \right| ; \quad (1)$$

$$\epsilon = \frac{1}{2} \left| \left(\frac{V_0}{V} \right)^{2/3} - 1 \right| = \eta \left(\frac{V_0}{V} \right)^{2/3} . \quad (2)$$

where V_0 and V are the initial and final specific volumes. As Truesdell and Noll^[8] have shown, the Lagrangian or the "material" strain is rotationally invariant, i.e., invariant under changes of the frame of reference, whereas the Eulerian or "spatial" strain does not in general satisfy this invariancy criterion. Hence, to overcome this limitation of ϵ , Davies^[6] has emphasized that the frame indifferent analogue, E , of the Eulerian strain ϵ should be used rather than ϵ . However, for the special case of isotropic bodies under hydrostatic pressure $E \equiv \epsilon$ and the invariancy condition is trivially satisfied. Thus for the liquids in our hydrostatic pressure experiments, one can conveniently describe a frame-invariant strain at any pressure in either the Lagrangian representation or the Eulerian frame - indifferent analogue representation (which here is identically equal to Eulerian strain). These strains can be evaluated by using an appropriate equation of state to

extrapolate and interpolate experimental P-V data to cover our entire 14 kbar accessible pressure range.

EQUATIONS OF STATE

The equations of state, for liquids and solids, that are widely used in the literature^[9,10] contain two or three parameters; bulk modulus plus first and sometimes second pressure derivatives of the bulk modulus. Since these constants cannot always be obtained with high accuracy from even the best available data^[9], they were evaluated for our studies by least squares fitting each equation of state to literature P-V data for each liquid. The standard error of estimate of each fitting was used as an indication of the ability of each equation of state to describe that particular liquid. In addition, where more than one source of P-V data was available for a liquid, the standard error was used to rank the reliability of each P-V data set.

RESULTS AND DISCUSSION

Table I presents some of the experimental results obtained on a number of liquids by the high pressure interferometric method^[4,11]. In every case except n-pentane the maximum pressures listed were determined by the freezing of the liquid at the stated temperature. Figure 1 shows a representative graph of Δn vs strain, for water evaluated from the P-V data of Adams^[12] and the 2nd-Order Murnaghan equation of state. It is seen that Δn increases truly linearly with the strain parameter E for the entire stability field of water in the liquid phase, but that Δn vs η is linear only below about 3% strain. Similar results were obtained with every liquid studied thus far. It is found that the range of linearity between Δn and strain is much larger when using the strain E instead of η . This is true for each and all equations

of state fitted to all P-V data of all the liquids studied. (Note that we will later show that three equations of state gave truly linear plots of Δn vs E over the entire 14 kbar pressure range for all liquids studied).

An important result of this work is that we have experimentally shown for the first time that E is a more useful strain measure than the Lagrangian strain η . Identical conclusions for the usefulness of E over η were theoretically deduced by Davies^[6] from both the ultrasonic data on the pressure dependence of the elastic moduli and the Hugoniot shock wave data for MgO.

Table II compares the fit of Δn for water to various degrees of polynomials in E for six of the widely used equations of state discussed in the literature. It is seen that a good linear relation between Δn and E is obtained with the Tait, 2nd-Order Murnaghan, 2nd-Order Birch, and Keane equations of state as evidenced by the value of the sum of the squares of the residuals as well as the standard error of estimate. The other equations, including those not listed there (such as Bridgman equation, etc.) yield poor linear fit and require higher order polynomials in E.

Similar analysis with the other liquids show that only three equations of state give a good linear relation of Δn with respect to E for all liquids. They are the 2nd-Order Murnaghan, 2nd-Order Birch, and the Keane equations of state. Anderson^[13], and Chhabildas and Ruoff^[14] have shown that of all the equations of state reported in the literature, only the Keane's equation yields physically as well as thermodynamically meaningful values on extrapolation to very high pressures. Hence the Keane equation is preferred over the other two that gave linear Δn vs E plots.

It is one of the more important results of our experiments that a single equation of state, Keane's equation, is found to give an excellent linear fit between Δn and E for all the liquids studied, irrespective of the nature of

the liquid, whether polar or nonpolar and whether composed of spherically symmetric, or planar, or long chain molecules and even though the volume strain involved is as high as 33%.

The linear Δn vs E relationship implies nonlinear relationship between Δn and volume strain and thus failure of Gladstone-Dale, Drude, Lorentz-Lorenz, Eykman equations since these equations assume constancy of polarizability. The present studies clearly indicate that polarizability is dependent on the volume. This aspect will be dealt with in detail elsewhere.

CONCLUSION

Interferometric measurements on a number of liquids at high pressure (to 14 kbars) show (i) first experimental proof that the Eulerian frame-indifferent analogue strain E is a more useful strain measure than the Lagrangian strain, (ii) Keane's equation of state best describes each and all liquids studied, (iii) change in refractive index vs E is linear for all liquids, even though the volume strain involved is as high as 33%.

ACKNOWLEDGEMENT

The authors would like to express their sincere thanks to Mr. G. R. Mariner for the numerous discussions.

NOTATION

A, B, C = constants

E = frame indifferent analogue of the Eulerian strain ϵ

n_0 = refractive index at STP

Δn = change in refractive index

P = hydrostatic pressure

V = specific volume at pressure P

V_0 = initial specific volume

ΔV = change in volume

ϵ = Eulerian strain

λ = wavelength of light

η = Lagrangian strain

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* Work supported by the Office of Naval Research, Physics Program.

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FIGURE CAPTION

Figure 1. Variation of refractive index of water with Lagrangian strain η , and strain parameter E .

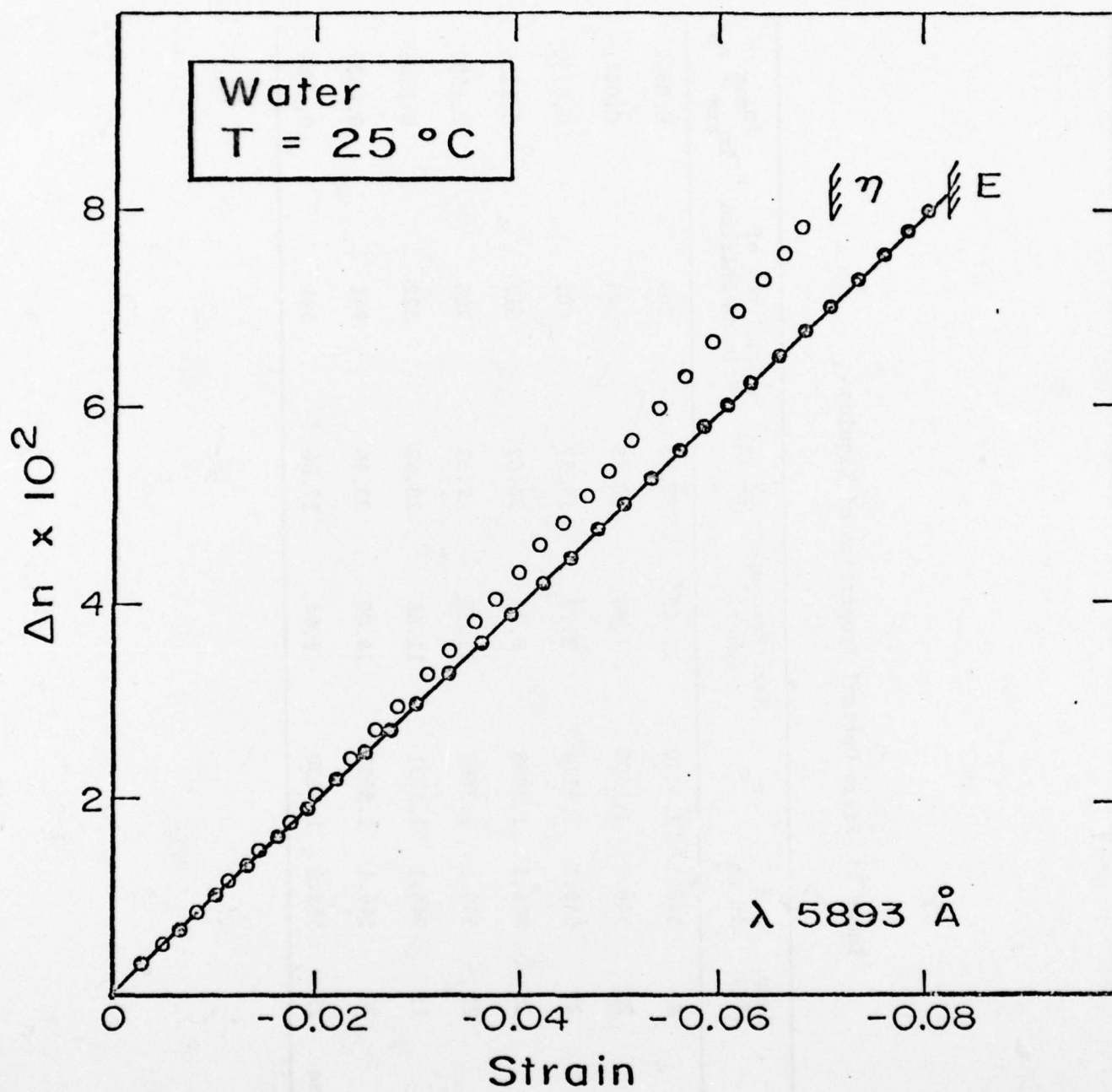


Table I: Piezo-Optical Properties of Liquids.

Liquid	Temp. (°C)	λ in nm	n_o	Max. Pressure (kbar)	$\frac{\Delta V}{V_o}$ (%)	Total no. of Fringes Shifted	Δn_{\max} ($n_{\max} - n_o$)
water	25	546.1	1.3340	11.43	20.98	369	0.0842
CCl ₄	25	546.1	1.4600	1.94	10.85	324	0.0671
n-decane	25	546.1	1.4114	3.23	14.37	402	0.0730
n-octane	25	546.1	1.3968	6.23	20.02	517	0.1116
n-heptane	25	546.1	1.3867	11.50	27.39	788	0.1507
n-hexane	25	546.1	1.3751	11.66	28.62	822	0.1566
n-pentane	30	546.1	1.3535	14.00	33.66	941	0.1809
chlorobenzene	25	589.3	1.5230	6.64	17.86	591	0.1188

Table II: Least-Squares Fitting Results for Water Using Adams P-V Data to Compute E; Δn Measured at 25°C Using $\lambda 589.3$ nm.

Equation	$\Delta n = A + BE + CE^2$			Sum of Squares of Residuals	Standard Error
	A	B	C		
Tait	-2.50×10^{-4}	-0.990	-0.016	4.43×10^{-7}	8.74×10^{-5}
	-2.69×10^{-4}	-0.991		4.38×10^{-7}	8.77×10^{-5} *
1st-Order Murnaghan	-1.06×10^{-4}	-0.987		7.54×10^{-7}	11.40×10^{-5}
	-0.07×10^{-4}	-0.980	-0.085	6.26×10^{-7}	10.48×10^{-5}
2nd-Order Murnaghan	-1.80×10^{-4}	-0.988		3.47×10^{-7}	7.74×10^{-5}
	-1.45×10^{-4}	-0.986	0.031	3.31×10^{-7}	7.62×10^{-5}
1st-Order Birch	-2.90×10^{-4}	-0.990		7.12×10^{-7}	11.08×10^{-5}
	-3.59×10^{-4}	-0.995	-0.058	6.53×10^{-7}	10.70×10^{-5}
2nd-Order Birch	-1.82×10^{-4}	-0.989		4.21×10^{-7}	8.52×10^{-5}
	-1.43×10^{-4}	-0.986	0.033	4.01×10^{-7}	8.39×10^{-5}
Keane	-1.85×10^{-4}	-0.989		4.44×10^{-7}	8.75×10^{-5}
	-1.48×10^{-4}	-0.986	0.032	4.26×10^{-7}	8.65×10^{-5}

* In least square analysis of nonlinear systems standard error of estimate does not necessarily decrease as the number of adjustable parameters is increased (see D. W. Marquardt, J. Soc. Indust. Appl. Math. 11, 431 [1963]).

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liquids, even though the volume strain involved is as high as 33%. This conclusion appears to be valid for all the liquids studied thus far.

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